



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NL96/00246 <b>(22) International Filing Date:</b> 14 June 1996 (14.06.96)  <b>(30) Priority Data:</b> 1000581                      16 June 1995 (16.06.95)                      NL  <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> JACOBS, Martinus, Jo- hannes, Nicolaas [NL/NL]; J. Van Maurikstraat 4, NL- 6416 EH Heerlen (NL). BACH, Elke [DE/DE]; Franken- ring 2, D-47798 Krefeld (DE). SCHOLLMeyer, Eckhard [DE/DE]; Frankenring 2, D-47798 Krefeld (DE). CLEVE, Ernst [DE/DE]; Frankenring 2, D-47798 Krefeld (DE).  <b>(74) Agent:</b> DERKS, Wilhelmus, Hubertus, Petrus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i> <i>In English translation (filed in Dutch).</i>
<b>(54) Title:</b> PROCESS FOR DYEING OF HIGHLY ORIENTED HIGHMOLECULAR-WEIGHT POLYETHYLENE MOULDED ARTI- CLES AND ARTICLES  <b>(57) Abstract</b>  The invention relates to a process for the dyeing of a highly oriented moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol. The invention also relates to dyeing of articles containing such a moulded article and to moulded articles and articles that can be obtained by these processes. In the process according to the invention the moulded article is contacted, at a temperature between 100 and 130 °C to a supercritical liquid in which a dye is dissolved.		

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PROCESS FOR DYEING OF HIGHLY ORIENTED HIGHMOLECULAR-WEIGHT POLYETHYLENE  
MOULDED ARTICLES AND ARTICLES.

10           The invention relates to a process for the  
dyeing of a highly oriented moulded article  
substantially consisting of a polyethylene having a  
weight average molecular weight of at least 400 kg/mol.  
The invention also relates to the dyeing of articles  
15   containing such a moulded article and to moulded  
articles and articles that can be obtained by these  
processes.

          A process of the same kind is described in  
JP-A-03.277.464. In the known process, highly oriented  
20   ultra-high molecular weight polyethylene fibres are  
contacted with a dye bath at a temperature of 100-130°C  
for 20-60 minutes, with the dye bath consisting of an  
aqueous dispersion of a finely ground mixture of  
specific dyes and surfactants whereupon the mould is  
25   washed and dried. For good dyeing results the fibres  
are preferably modified by means of a plasma or corona  
treatment prior to the dyeing operation.

          An important drawback of the known process is  
that the dyed fibres, particularly if they are not  
30   first modified by means of a plasma or corona  
treatment, possess insufficient colour intensity and  
that the colour has insufficient resistance to rubbing  
and washing due to the dyes being located substantially  
at the surface of the fibres.

35           The object of the invention is to provide a  
process that exhibits the aforementioned drawbacks to a  
lesser degree.

This object is achieved by the invention in that the moulding is contacted, at a temperature of between 100 and 130°C, with a supercritical liquid in which a dye is dissolved.

5           It has been found that very good dyeing results can be achieved by using the process of the invention. The dyes are brought into the moulding to a greater depth so that they cannot be removed, or can be removed only with great difficulty, by washing with  
10 water, by rubbing or even by boiling in hexane. A further advantage of the process of the invention is that the process is less laborious because no elaborate washing step or drying step is needed after dyeing. Yet another advantage is that the mouldings are coloured  
15 more uniformly. It has specifically been found that good coloration occurs even in places that are difficult of access or inaccessible to dyes dispersed in water, such as those places where fibres are wound one over the other. This affords the highly attractive  
20 possibility of colouring fibre bobbins in their entirety.

          As supercritical liquid the therefore known and suitable substances suitable for the purpose may be used, such as carbon dioxide, dinitrogen oxide,  
25 ammonia, ethane or propane. Preferably, the supercritical liquid is carbon dioxide inasmuch as this substance becomes supercritical at a relatively low temperature and pressure and is harmless to man and the environment.

30           The choice of dye is of great importance. The dye must on the one hand obviously be soluble in the supercritical liquid and on the other exhibit a good affinity to highly oriented high-molecular-weight polyethylene mouldings. Good affinity means that the  
35 dye, in supercritical dyeing, is well able to penetrate into the moulding, resulting in a high colour intensity and high resistance to rubbing and washing.

It has been found that dye molecules which are essentially plate-shaped exhibit a good affinity. The shape of the dye molecule is defined on the basis of a rectangular box, which box tightly envelopes the dye molecule, with the molecule having a configuration with minimum energy content (in vacuo). By the molecular length, width and depth is meant the length, width and depth of the enveloping box.

The configuration with minimum energy content in vacuo can be determined with the aid of the Biosym Software molecular modelling package (release 23.7). This package makes it possible to construct the molecule in a random, preferably as elongate a shape as possible, whereupon the molecule configuration is so adapted by an iterative process as to minimize the energy content. A CVFF force field is used and optimization is continued until a maximum energy gradient of 0.0001 Kcal/molÅ is obtained. If there are several configurations having a local minimum in energy content, the configuration having the lowest energy content is chosen.

The molecular length is the longest dimension of the (energy-minimized) molecule. In determining the dimension, only the distances between the atoms are measured and no account is taken of the radius of the atom. The molecular width is determined by determining in a projection of the molecule along the molecular longitudinal axis the longest dimension at a right angle to the longitudinal axis. The molecular depth is determined by determining the longest dimension in a projection of the molecule along the plane formed by the longitudinal and the latitudinal axis at a right angle to the plane.

It is preferred for plate-shaped dye molecules to be used in the process of the invention, which means that the molecular depth of the dye molecule is at most 0.5 nm. More preferably, the

molecular depth is at most 0.4 nm, still more preferably at most 0.3 nm and most preferably at most 0.2 nm. A depth of 0.2 nm corresponds to a perfectly flat molecule. Preferably, the product of the molecular  
5 depth and the molecular width of the dye molecule is at most 0.4 nm<sup>2</sup>, more preferably at most 0.3 nm<sup>2</sup>.

Another criterion by which good dyes can be distinguished from inferior dyes is that all atoms in the dye molecule having an sp<sup>3</sup> hybridization contain at  
10 most 2 substituents whose largest molecular dimension is greater than 0.5 nm.

Preferably, the dye also has a molecular weight of at most 1000 g/mol. On the one hand, at higher molecular weights the solubility in  
15 supercritical solvents, particularly in supercritical CO<sub>2</sub>, deteriorates. On the other hand, the polyethylene moulded article's affinity to colouring is lower. Dyes having a molecular weight below 250 g/mol are readily absorbed by the polyethylene moulded article but can  
20 also be removed from the moulded article relatively easily. This problem can be resolved for instance by chemically fixing such dyes in the moulded article. Preferably, the molecular weight of the dye used in the process of the invention is at least 250 g/mol.

25 Good results are achieved if the dye is an azo compound with the formula Ar-N=N-Ar, where Ar is an aryl group, which may or may not be substituted. Aryl group is understood to be a benzyl or a naphthyl group in particular. Such azo compounds, on account of their  
30 rigid configuration, are plate-shaped and have good affinity to the polyethylene moulded article.

Suitable dyes are the said azo compounds in which an Ar is substituted in the para position with an (-NH-C(=O)-R) group in which R is an alkyl, aryl or  
35 hydrogen. The amide group forms a semi-rigid, plate-shaped configuration with the azo compound.

Particularly suitable dyes are azo compounds

in which an Ar is substituted in the para position with an (-N=N-Ar) group in which Ar is an aryl group, which may or may not be substituted. Such diazo compounds, on account of their rigid configuration, are plate-shaped and have very good affinity to the polyethylene moulded article.

In the light of the plate shape of the dye molecule aimed at, the substituents in the ortho and meta positions of the aryl groups Ar of the azo and diazo compounds mentioned preferably have a greatest molecular dimension of at most 0.5 nm. Dye molecules having, for instance, an aryl group or a chain of more than 4 successive atoms (ignoring hydrogen atoms) as substituents in ortho and meta positions exhibit a lower affinity to the polyethylene moulded article. For obtaining high lightfastness it is preferred for the azo diazo compounds not to have any amine substituents linked to the Ar groups. Lightfastness here means a colour's resistance to change on being irradiated with UV light as described in DIN 64004.

The dye must be soluble in the supercritical liquid at the specified conditions of temperature and pressure. If the solubility of the dye is inadequate, it may be improved by adding moderators to the supercritical liquid. Moderators are for example toluene, methylpyrrolidone, Decalin, glycols or propanol.

However, a drawback of adding moderators is that they may be left behind on or in the polyethylene moulded article on removing the supercritical liquid. This involves the risk of the moderators having an adverse effect on the properties of the moulded article. A further drawback is that the moderators are often toxic, flammable and/or explosive. As a result, the important advantage of supercritical carbon dioxide that the solvent can be vented into the atmosphere without any safety precautions is lost. Surprisingly,

it has been found that dyes having a solubility in acetone of at least 0.2 g/l at room temperature are well soluble in supercritical carbon dioxide without the use of moderators. In the most-preferred process,  
5 the supercritical solvent is carbon dioxide and the dye has a solubility in acetone of at least 0.2 g/l at room temperature.

A general description of a process for incorporating additives, including dyes, in polymeric  
10 fibres with the aid of a supercritical liquid is given in EP-B-0222207. It states that the polymeric fibre must assume a swollen condition in order to be able to incorporate the additives in the fibre, the degree of swelling of the fibre being at least 2 vol.% and  
15 preferably 5 vol.%.

In the process of the invention the degree of swelling of the fibres during supercritical dyeing preferably is less than 1 vol.%. The degree of swelling is defined as the extent of the fibre's increase in volume on being  
20 contacted with a supercritical liquid. The advantage of this is that the strength of the fibre does not diminish unacceptably. A swelling degree of less than 1 vol.% is achieved by choosing a suitable supercritical liquid, for example CO<sub>2</sub>, and a temperature below 130°C.  
25 The process described in EP-B-0.222.207, in which the degree of swelling is greater than 2 vol.% and preferably greater than 5 vol.%, cannot be applied because at a degree of swelling of 2 or 5 vol.%, if such a degree of swelling could occur at all, the  
30 fibres almost completely lose their strength. Generally speaking, fibres having a crystallinity higher than 80% and a tensile strength greater than 2.5 GPa swell by less than 1 vol.% on being contacted with a supercritical liquid.

35 Moulded article includes in particular fibres, monofilaments, multifilament yarns, staple fibre yarns, tapes, strips and films. The moulded



article preferably is a fibre.

Highly oriented means that the moulded articles have been drawn so that the polymer chains run substantially completely parallel with the direction of drawing. It is preferred for the degree of orientation  $F$  to be at least 0.90, more preferably at least 0.95. The degree of orientation is defined by the formula  $F = (90^\circ - H^\circ/2)90^\circ$ , where  $H^\circ$  is the width at half the height of the scattering intensity along the Debye ring of the strongest reflection on the equator. Moulded parts of highly oriented polyethylene have a high crystallinity of at least 70%, preferably of at least 80% and a tensile strength of at least 1,2 GPa and a tensile modulus of at least 40 GPa. Because of their high orientation and crystallinity, such moulded parts are not dyeable or are poorly dyeable by the processes known to date.

Ethylene homopolymer and copolymers of polyethylene and polypropylene are particularly suitable for use as polyethylene. The polyethylene used may also contain small amounts of one or more other polymers, particularly other alkene-1-polymers.

Preferably, the moulded article is a high-molecular-weight linear polyethylene fibre having a tensile strength of at least 1.2 GPa and a tensile modulus of at least 40 GPa. High-molecular weight means a molecular weight of at least 400,000 g/mol.

Linear polyethylene here means polyethylene with fewer than 1 side chain per 100 C atoms, preferably fewer than 1 side chain per 300 C atoms. Furthermore, the polyethylene may contain up to 5 mol.% of one or more other alkenes that can be copolymerized with it, such as propylene, butene, pentene, 4-methylpentene, octene.

Preferably, use is made of polyethylene fibres consisting of polyethylene filaments that have been prepared by a gel spinning process as described in

for instance GB-A-2042414 and GB-A-2051667. Basically, this process comprises preparing a solution of a polyethylene having a high intrinsic viscosity, spinning the solution to filaments at a temperature  
5 above the dissolution temperature, cooling the filaments below the gelating temperature so that gelation takes place and drawing the filaments before, during or after removal of the solvent.

The shape of the cross section of the  
10 filaments can in that process be chosen by the choice of the shape of the spinning opening.

The preparation of a highly oriented polyethylene moulded article usually includes two or more drawing steps, often at progressively higher  
15 temperature and lower drawing rates.

In another embodiment of the process of the invention the moulded article is redrawn after dyeing. Surprisingly, it has been found that the colour intensity is enhanced by the drawing itself. A good  
20 enhancement of the colour intensity can in principle be achieved in a drawing operation that does not or does not substantially contribute to the strength or modulus, for example at most 20 or 10%. However, from a process engineering point of view it is advantageous to  
25 carry out the drawing operation such that the strength and modulus are also further improved. The manner in which this can be achieved is known to one skilled in the art. The presence of dyes has no adverse effect on the tensile strength and tensile modulus attainable by  
30 drawing. A further advantage of this embodiment even is that the dyed moulded articles obtained have a higher tensile strength and tensile modulus than moulded articles that are drawn under comparable conditions and are dyed afterwards.

35 In a preferred embodiment of the above process a solvent for polyethylene is applied to the moulded article prior to or during drawing. The

advantage of this is that the colour intensity increases further. Preferably, this solvent is a non-volatile substance such as paraffin oil. The advantage of this is that the solvent concentration remains  
5 virtually constant during drawing.

A good colour intensity can be obtained by drawing the dyed moulded article, whether or not in the presence of a solvent, even if the moulded article is ultrahighly oriented prior to drawing and/or if dyes  
10 are used that give too weak a colour intensity without these measures. Ultrahighly oriented moulded article here and hereafter means a moulded article having a tensile strength of at least 2.5 GPa, preferably at least 3 GPa and more preferably 3.5 GPa.

15 In another embodiment of the process the moulded article is a polyethylene fibre whose tensile strength prior to drawing is between 0.7 GPa and 2.5 GPa. More preferably, the tensile strength then is between 0.7 and 2 GPa, more preferably between 0.7 and  
20 1.5 GPa. It has been found that, with this measure, a still higher colour intensity can be obtained. In this case, the moulded article is preferably drawn after dyeing to a strength of at least 2.5 GPa, preferably at least 3 GPa, still more preferably 3.5 GPa.

25 The tensile strength of the moulded article preferably is at least 0.7 GPa, because the moulded article needs to have a certain minimum strength so that it can be used under high pressure and temperature conditions.

30 The drawing may take place in a wide temperature range. At low temperatures, however, the drawing rate should be low in order to prevent premature breakage. If a higher drawing rate is to be obtained, the drawing temperature is preferably chosen  
35 within 10°C below the melting point of the moulded article and the drawing rate is below 1 sec<sup>-1</sup>. For dyes with a low molecular weight, lower than, say, 300 g/mol

or more particularly lower than 250 g/mol, the post-drawing temperature is preferably chosen so low that sublimation or sweating of the dye out of the fibre remains limited.

5 Surprisingly, it has been found that highly oriented polyethylene moulded articles, especially fibres, obtain a higher colour intensity if they undergo a mechanical operation prior to dyeing. Mechanical operation particularly means exposing the  
10 fibres to a flexural load in such a way that a component force acts on the fibre perpendicularly to the direction of the fibre. This situation arises when for instance a taut fibre is pulled through an eye at a certain bending angle. In an still better embodiment of  
15 the process of the invention the moulded article is therefore exposed to a flexural load prior to being dyed. The extent of loading, which is determined by the stress and the angle at which the stress is exerted, is on the basis of the desired compromise between  
20 the colour intensity and an acceptable strength retention.

Since, almost without exception, a flexural load also occurs in the processing of a fibre to an article by, for instance, taslanization, crimping,  
25 twisting, doubling, weaving, knitting or braiding, the aforementioned advantages are also obtained when the polyolefinic moulded articles are dyed after they have been incorporated into an article.

The invention therefore also relates to a  
30 process for dyeing articles containing a highly oriented moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol, characterized in that the moulded article is contacted, at a temperature of  
35 between 100 and 130°C, with a supercritical liquid in which a dye is dissolved. Some examples of such articles are blended yarns, combined yarns, knitted

fabrics, woven fabrics, felts, ropes, fishing lines, sails, gloves and helmets.

The aforementioned preferred embodiments for the dyeing of a polyethylene moulded article are analogously applicable to the dyeing of articles containing such moulded articles.

In an embodiment of the aforementioned process that is particularly preferred the article, more specifically a rope or a fishing line, substantially consists of partially drawn polyethylene fibres having a tensile strength of at least 0.7 GPa and a tensile modulus of at least 7 GPa and the article is post-drawn after dyeing. Further advantages of the latter embodiment are that loss in strength caused by assembly of the article from the polyethylene fibres by for instance twisting, plying or braiding is offset in the post-drawing step so that the article has both a higher colour intensity and a much higher strength and dimensional stability.

The temperature in the process of the invention is from 100 to 130°C. Below 100°C, the solubility of the dyes in the supercritical liquid, especially in carbon dioxide, is too low. Above 130°C, excessive shrinkage and strength loss occurs in the polyethylene moulded parts. In order to alleviate strength losses it is preferred for the moulded articles to be dyed as they are taut. A suitable method of dyeing taut fibres is to tightly wind a number of layers of the fibres onto a bobbin and then to dye them.

The pressure is chosen in dependence on the liquid used. For supercritical carbon dioxide the pressure preferably is at least 20, more preferably at least 25 MPa. The solubility of the dyes is higher at such high pressures. After dyeing, the pressure preferably is reduced at a rate of at most 1.5 MPa per minute, more preferably at most 1 MPa per minute. If

the pressure is reduced discontinuously, the pressure is reduced in each step preferably by not more than 1.5 MPa, preferably not more than 1 MPa, with the intervals between each step being long enough not to exceed the  
5 said highest rate of pressure reduction. It has been found that too rapid pressure reduction may lead to damage to the moulded article. Too rapid expansion may lead to significant strength loss especially in partially drawn polyethylene fibres with a low tensile  
10 strength (between 0.7 and 2 GPa).

The dyeing time is so chosen that the colour intensity is as high as possible. In general, no appreciable improvement in colour intensity is obtained after a dyeing time of 5 minutes, particularly after 10  
15 minutes. The amount of dye weighed into the moulded article generally amounts to from 0.1 to 5 wt.% relative to the weight of the moulded article. Preferably, a somewhat larger amount of dye is added than the amount which is soluble in the supercritical  
20 liquid. Preferably, the solution is stirred in order to obtain good, homogeneous coloration.

Besides the dyes, other substances may optionally be added to the supercritical solvent; these include UV stabilizers for improving the light-fastness  
25 of the dyes or crosslinking reagents for improving the creep resistance and the oxystability of the polyethylene moulded articles.

Mixtures of the basic dyes yellow, blue and red may be used in a manner known in the art in order  
30 to obtain different colours.

A detailed process for supercritical dyeing is described in Text. Res. J. 63(3, 135-142 (1993).

The invention will now be illustrated by some examples.

35 The following polyethylene moulded articles were dyed:

A: High-drawn (HD) yarns consisting of linear polyethylene with an ultrahigh molecular weight, marketed with the tradename Dyneema SK60

5 B: Partially drawn (PD) yarns consisting of linear polyethylene with an ultrahigh molecular weight, obtainable with a strength of about 1 GPa and a modulus of 13 GPa.

The yarns were wound onto a perforated stainless steel cylinder and placed in an autoclave.  
10 The dyes were added on the bottom of the autoclave in the form of a powder. The apparatus was purged of air by means of carbon dioxide and was then heated. After the operating temperature was reached the carbon dioxide, while being stirred, was isothermically  
15 brought to the operating temperature. The pressure and the temperature were kept constant during the dyeing time. After the dyeing time the pressure was released at a rate of about 1 MPa per minute.

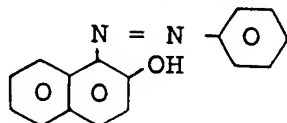
The amount of dye was 1% relative to the yarn  
20 weight, the pressure was 26 MPa, the temperature was 120°C and the dyeing time was 30 min.

The coloured fibres so obtained were visually assessed as to colour intensity. The table below gives the tradenames and the structural formulae of the dyes  
25 as well as an indication of the colour intensity ((P = poor, M = moderate, G = good, VG = very good) for both HD and PD yarns. The rating "poor" does not suggest that coloration did not occur or might not occur with further improvement measures it as described above.

Tabel 1: de geteste kleurstoffen

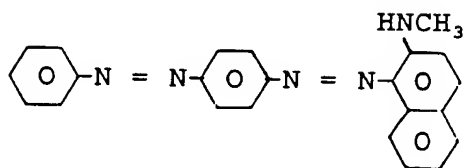
## 1. Solvent Yellow 14 (Sudan I)

5



## 2. Lipid Crimson

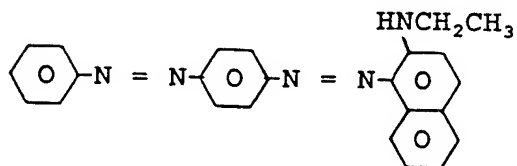
10



15

## 3. Solvent Red 19 (Fettrot B)

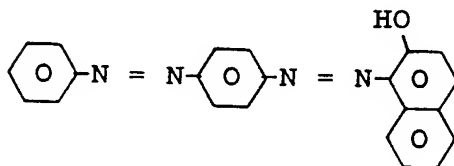
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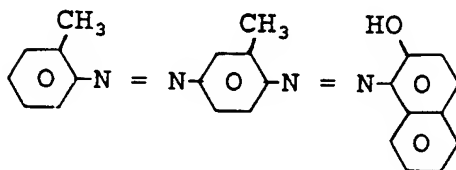
## 4. Solvent Red 23

30



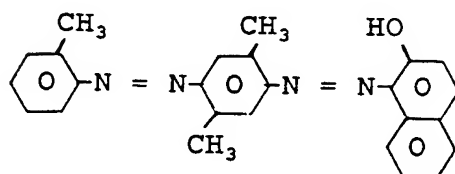
## 5. Solvent Red 24

40



## 6. Solvent Red 26

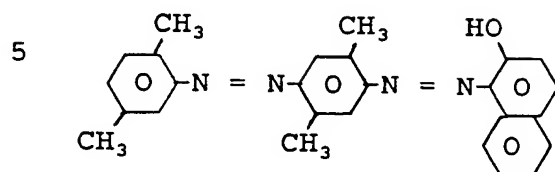
50



HVG	PVG
ZG	ZG
ZG	ZG
ZG	ZG
G	ZG
G	ZG
ZG	ZG

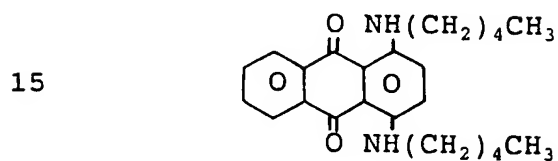


## 7. Solvent Red 27

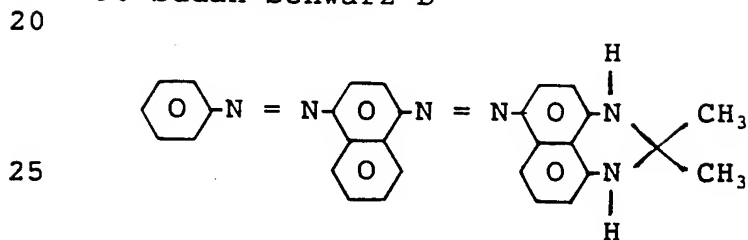


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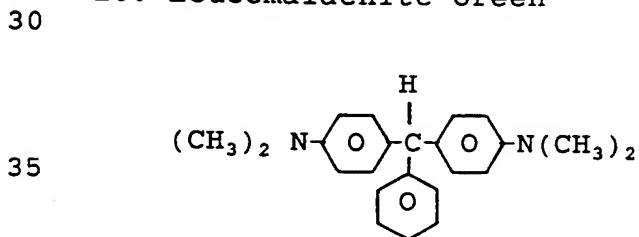
## 8. Solvent Blue 14



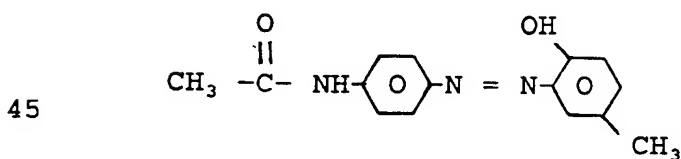
## 9. Sudan Schwarz B



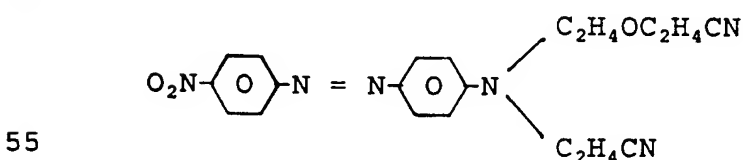
## 10. Leucomalachite Green



## 11. DTNW 11



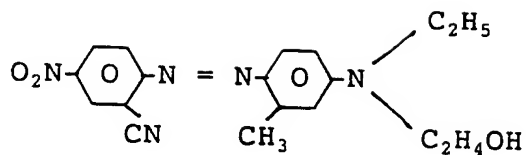
## 12. DTNW 13



HVG	PVG
G	ZG
M	G
M	G
S	S
G	ZG
S	M

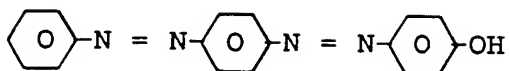
5 13. DTNW 19

10



15 14. DTNW 20

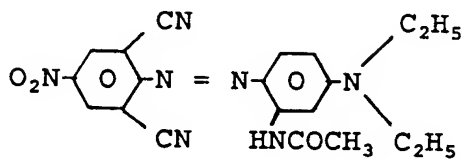
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30 15. DTNW 21

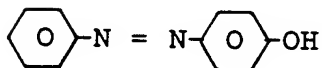
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45 16. Solvent Yellow 7

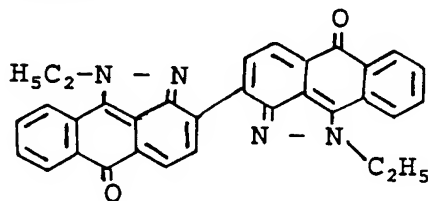
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60 17. DTNW 2

65



HVG	PVG
M	G
M	M
M	G
ZG	ZG
S	S

The molecular dimensions of some of the dyes included in Table 1 are given in Table 2. Figure 1 shows by way of illustration how the molecular dimensions of dye number 10 were determined.

5

10

dye	L	B	D	A	INT (HD/PD)
3	18.4	10.2	1.8	18.4	VG/VG
8	19.49	12.7	1.8	22.4	M/G
10	12.9	12.9	5.4	69	P/P
12	18.9	11.5	3.0	34.5	P/M
17	18.3	11.0	3.8	42	P/P

The table shows that molecules having too large a molecular depth exhibit poor affinity to the moulded article.

In all cases, the colour intensity of the PD yarns was higher than that of HD yarns. The dyed fibres obtained are all highly rubfast. Dyes 1 and 16, having a molecular weight of 248 and 200, respectively, give a very good colour intensity but, owing to their low molecular weight, present the drawback that they readily diffuse from the fibres. Washfastness was very good in all other cases. Dyes Nos. 10, 12 and 17 give poor or moderate colour intensity on account of their molecular depth being too large. Of dye 9 (Sudan black) only the blue component was absorbed well. The colour intensity indicators relate to blueing.

The azo compounds, especially dyes 3-7, also prove to have very good lightfastness in accordance with DIN 64004, the lightfastness of the PD years being the highest in all cases.

Dyes 3 to 7 had an acceptable lightfastness level of 2 or 3 for the HD yarns and a good lightfastness of 3 to

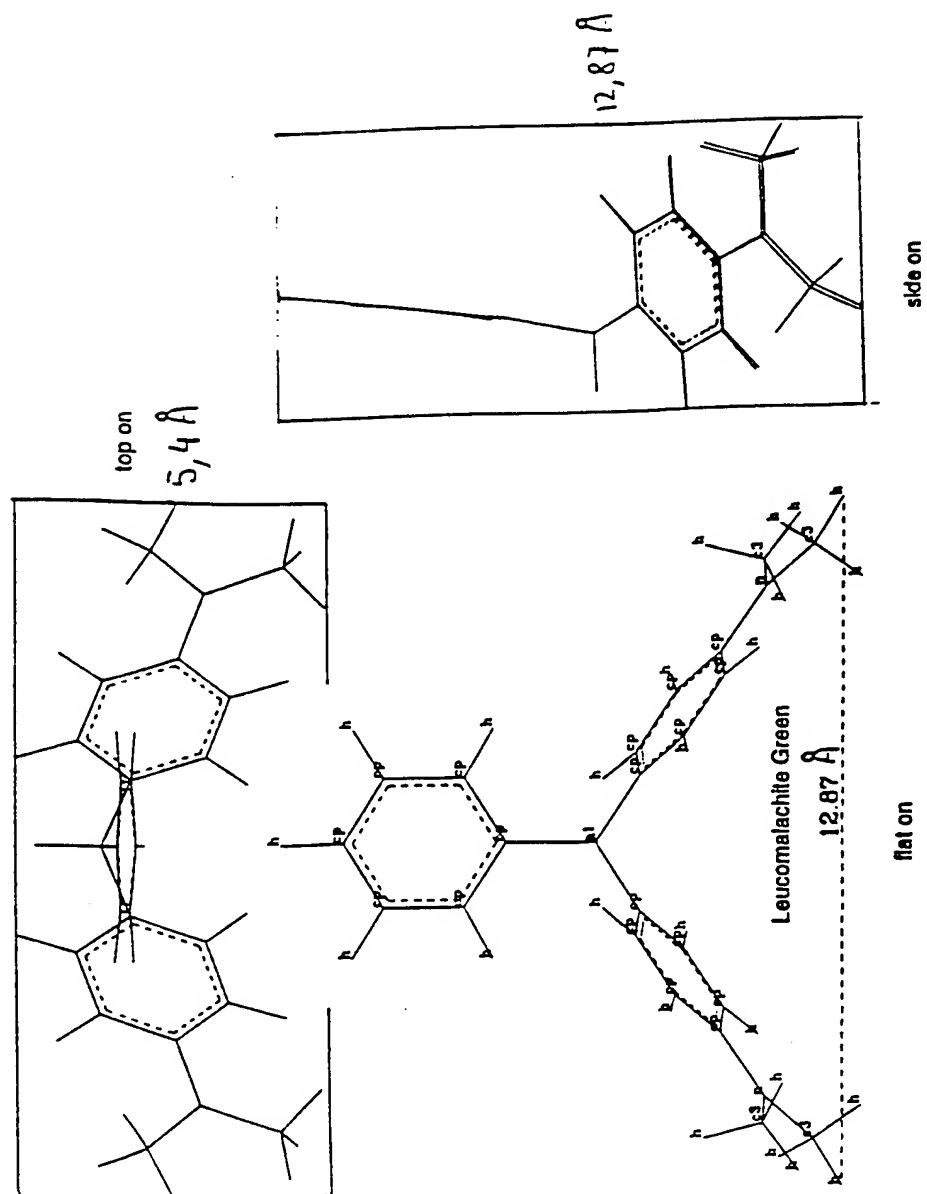
4 for the PD yarn. Dye 2 had a moderate to poor lightfastness of 1 for both HD and PD yarns. A good colour intensity and a surprisingly high lightfastness (4) were obtained with the dye CO<sub>2</sub>-PES Blau (Ciba-Geigy) singly and in combination with dye 11 (green colour). The highest lightfastness (5) was obtained using a combination of CO<sub>2</sub>-PES Blau (Ciba-Geigy) in combination with dye 11 (DTNW 11) and a Chimasorb 90 UV stabilizer.

10           Comparable experiments using dinitrogen oxide as supercritical solvent yielded comparable results in most cases. As an exception, it was found that in supercritical dinitrogen oxide a higher colour intensity (darker green) was obtained when dyeing with  
15 a mixture of dye 9 (blue) and 11 (yellow).

Braided fishing lines and knitted fabrics produced from HD yarns were dyed in the manner described above using several dyes mentioned in Table 1. The colour intensity of the yarns in the articles  
20 was higher than the colour intensity of HD yarns that had not undergone any treatment.

By way of Comparative Experiment HD and PD yarns were subjected to a dyeing treatment for 30 minutes using a solution of dye 4 in N-heptane and  
25 acetone at room temperature as well as at the boiling point of the solvent. In all cases, coloration was superficial and non-uniform. The dye could be removed almost completely from the fibres' surface by light rubbing and by washing with n-heptane and acetone at  
30 room temperature.

Figure 1: Determination of molecular dimensions on dye 10 (Leucomalachite Green)



C L A I M S

1. Process for the dyeing of a highly oriented moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol, characterized in that the moulded article is contacted, at a temperature of between 100 and 130°C, with a supercritical liquid in which is dye has been dissolved.
2. Process according to claim 1, characterized in that the supercritical liquid is carbon dioxide.
3. Process according to claim 1 or 2, characterized in that the molecular depth of the dye molecule is at most 0.5 nm.
4. Process according to any one of claims 1-3, characterized in that the product of the molecular depth and the molecular width of the dye molecule is at most 0.4 nm<sup>2</sup>.
5. Process according to any one of claims 1-4, characterized in that the dye has a molecular weight of at most 1000 g/mol.
6. Process according to any one of claims 1-5, characterized in that the molecular weight of the dye is at least 250 g/mol.
7. Process according to any one of claims 1-6, characterized in that the dye is an azo compound according to the formula  $\text{Ar-N=N-Ar}$ , where Ar is an aryl group, which may or may not be substituted.
8. Process according to claim 7, characterized in that an Ar is substituted in the para position with an  $(-\text{NH}-\text{C}(=\text{O})-\text{R})$  group, in which R is an alkyl, aryl or hydrogen.
9. Process according to claim 7, characterized in that in the azo compound an Ar is substituted in the para position with an  $(-\text{N}=\text{N}-\text{Ar})$  group, in which Ar is an aryl group, which may or may not be

substituted.

10. Process according to any one of claims 7-9,  
characterized in that substituents in the ortho  
and meta positions of the aryl groups Ar of the  
5 azo and diazo compounds mentioned have a largest  
molecular dimension of at most 0.5 nm.
11. Process according to any one of claims 1-10,  
characterized in that the supercritical solvent is  
carbon dioxide and in that the dye has an acetone-  
10 solubility at room temperature of 0.2 g/l.
12. Process according to any one of claims 1-11,  
characterized in that the moulded article is a  
high-molecular-weight linear polyethylene fibre  
having a tensile strength of at least 1.2 GPa and  
15 a tensile modulus of at least 40 GPa.
13. Process according to any one of claims 1-11,  
characterized in that the moulded article is drawn  
after dyeing.
14. Process according to claim 13, characterized in  
20 that a solvent for polyethylene is applied to the  
moulded article prior to or during drawing.
15. Process according to claim 13 or 14, characterized  
in that the moulded article is an ultrahighly  
oriented polyethylene fibre having a tensile  
25 strength of at least 2.5 GPa prior to drawing.
16. Process according to claim 13 or 14, characterized  
in that the moulded article is a polyethylene  
fibre whose tensile strength prior to drawing is  
between 0.7 and 2.5 GPa.
- 30 17. Process according to any one of claims 1-16,  
characterized in that the moulded article is  
subjected to a flexural load prior to dyeing.
18. Dyed moulded articles obtainable by the process  
according to any one of claims 1-17.
- 35 19. Process for dyeing articles containing a highly  
oriented moulded article substantially consisting  
of a polyethylene having a weight-average

- 5 molecular weight of at least 400 kg/mole,  
characterized in that the article, at a  
temperature between 100 and 130°C, is contacted  
with a supercritical liquid in which a dye is  
dissolved.
- 10 20. Process according to claim 19, characterized in  
that the article, in particular a rope or fishing  
line, substantially consists of partially drawn  
polyethylene fibres having a tensile strength of  
at least 0.8 GPa and a tensile modulus of at least  
8 GPa and that the article is drawn further after  
dyeing.
21. Dyed articles obtainable according to claim 19 or  
20.



## AMENDED CLAIMS

[received by the International Bureau on 26 November 1996 (26.11.96); original claims 1,11,13 and 20 amended; remaining claims unchanged (3 pages)]

1. Process for the dyeing of a highly oriented moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol and having a crystallinity of at least 70%, characterized in that the moulded article is contacted, at a temperature of between 100 and 130°C, with a supercritical liquid in which a dye has been dissolved.
2. Process according to claim 1, characterized in that the supercritical liquid is carbon dioxide.
3. Process according to claim 1 or 2, characterized in that the molecular depth of the dye molecule is at most 0.5 nm.
4. Process according to any one of claims 1-3, characterized in that the product of the molecular depth and the molecular width of the dye molecule is at most 0.4 nm<sup>2</sup>.
5. Process according to any one of claims 1-4, characterized in that the dye has a molecular weight of at most 1000 g/mol.
6. Process according to any one of claims 1-5, characterized in that the molecular weight of the dye is at least 250 g/mol.
7. Process according to any one of claims 1-6, characterized in that the dye is an azo compound according to the formula  $\text{Ar}-\text{N}=\text{N}-\text{Ar}$ , where Ar is an aryl group, which may or may not be substituted.
8. Process according to claim 7, characterized in that an Ar is substituted in the para position with an  $(-\text{NH}-\text{C}(=\text{O})-\text{R})$  group, in which R is an alkyl, aryl or hydrogen.
9. Process according to claim 7, characterized in that in the azo compound an Ar is substituted in the para position with an  $(-\text{N}=\text{N}-\text{Ar})$  group, in which Ar is an aryl group, which may or may not be substituted.
10. Process according to any one of claims 7-9, characterized in that substituents in the ortho and meta positions of the aryl groups Ar of the azo and diazo compounds mentioned have a largest molecular dimension of at most 0.5 nm.

11. Process according to any one of claims 1-10, characterized in that the supercritical solvent is carbon dioxide and in that the dye has an acetone-solubility at room temperature of at least 0.2 g/l.
12. Process according to any one of claims 1-11, characterized in that the moulded article is a high-molecular-weight linear polyethylene fibre having a tensile strength of at least 1.2 GPa and a tensile modulus of at least 40 GPa.
13. Process for the manufacturing of a highly oriented, dyed moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol, characterized in that a moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol is contacted, at a temperature of between 100 and 130°C, with a supercritical liquid in which a dye has been dissolved and that the moulded article is drawn after dyeing.
14. Process according to claim 13, characterized in that a solvent for polyethylene is applied to the moulded article prior to or during drawing.
15. Process according to claim 13 or 14, characterized in that the moulded article is an ultrahighly oriented polyethylene fibre having a tensile strength of at least 2.5 GPa prior to drawing.
16. Process according to claim 13 or 14, characterized in that the moulded article is a polyethylene fibre whose tensile strength prior to drawing is between 0.7 and 2.5 GPa.
17. Process according to any one of claims 1-16, characterized in that the moulded article is subjected to a flexural load prior to dyeing.
18. Dyed moulded articles obtainable by the process according to any one of claims 1-17.
19. Process for dyeing articles containing a highly oriented moulded article substantially consisting of a polyethylene having a weight-average molecular weight of at least 400 kg/mole, characterized in that the article, at a

temperature between 100 and 130°C, is contacted with a supercritical liquid in which a dye is dissolved.

20. Process according to claim 19, characterized in that the article, in particular a rope or fishing line, comprises polyethylene fibres having a tensile strength of at least 0.7 GPa and a tensile modulus of at least 7 GPa and that the article is drawn further after dyeing.
21. Dyed articles obtainable according to claim 19 or 20.

## INTERNATIONAL SEARCH REPORT

Intern 11 Application No

PCT/NL 96/00246

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06P5/20 D06P3/79 D06P7/00 D01F6/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06P D06M D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 474 600 (CIBA GEIGY AG) 11 March 1992 see page 5, line 57 - page 6, line 3; claims; examples ---	1-11,18
X	EP,A,0 474 599 (CIBA GEIGY AG) 11 March 1992 see page 4, line 56 - page 5, line 2; claims ---	1-6,11, 18
X	EP,A,0 514 337 (CIBA GEIGY AG) 19 November 1992 see page 3, line 45 - line 58; claims; examples --- -/--	1-11,18

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 September 1996

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Intern Application No  
PCT/NL 96/00246

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	TEXTILE RESEARCH JOURNAL, vol. 63, no. 3, 1 March 1993, pages 135-142, XP000360491 SAUS W ET AL: "DYEING OF TEXTILES IN SUPERCRITICAL CARBON DIOXIDE" cited in the application see page 139, left-hand column, last paragraph ---	1-6,11, 18
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A	EP,A,0 009 765 (WIGGINS ALLAN A JR) 16 April 1980 see page 6, line 34 - page 7, line 1 ---	1,13, 18-21
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A	DATABASE WPI Section Ch, Week 9248 Derwent Publications Ltd., London, GB; Class A17, AN 92-392413 XP002013508 & JP,A,04 289 213 ( TOYOB0 KK) , 14 October 1992 see abstract ---	1,13,14, 18,20,21
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Information on patent family members

International Application No

PCT/NL 96/00246

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**PUB-NO:** WO009700353A1  
**DOCUMENT-IDENTIFIER:** WO 9700353 A1  
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ORIENTED HIGHMOLECULAR-  
WEIGHT POLYETHYLENE MOULDED  
ARTICLES AND ARTICLES  
**PUBN-DATE:** January 3, 1997

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**APPL-NO:** NL09600246  
**APPL-DATE:** June 14, 1996

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**INT-CL (IPC):** D06P005/20 , D06P003/79 , D06P007/00 ,  
D01F006/04

**EUR-CL (EPC):** D01F006/04 , D06P001/94 , D06P003/79 ,  
D06P007/00

**ABSTRACT:**

CHG DATE=19990617 STATUS=O>The invention relates to a process for the dyeing of a highly oriented moulded article substantially consisting of a polyethylene having a weight average molecular weight of at least 400 kg/mol. The invention also relates to dyeing of articles containing such a moulded article and to moulded articles and articles that can be obtained by these processes. In the process according to the invention the moulded article is contacted, at a temperature between 100 and 130 DEG C to a supercritical liquid in which a dye is dissolved.